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A Study of Compositions and  
Heat Treatment for the Development  
of the Ox Blood Red Glaze

Ceramic Engineering

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**A STUDY OF COMPOSITIONS AND HEAT  
TREATMENT FOR THE DEVELOPMENT OF  
THE OX BLOOD RED GLAZE**

BY

**WILLIAM OWEN RATHFON**

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**THESIS**

FOR THE

**DEGREE OF BACHELOR OF SCIENCE**

IN

**CERAMIC ENGINEERING**

---

**COLLEGE OF LIBERAL ARTS AND SCIENCES**

**UNIVERSITY OF ILLINOIS**

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June 1, 1915

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

William Owen Rathfon

ENTITLED A STUDY OF COMPOSITIONS AND HEAT TREATMENT FOR THE

DEVELOPMENT OF THE OX BLOOD RED GLAZE

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Ceramic Engineering

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1915  
R18

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A STUDY OF COMPOSITIONS AND HEAT  
TREATMENT FOR THE DEVELOPMENT OF  
THE OX BLOOD RED GLAZE

INTRODUCTION

The so-called ox blood red glaze, which is obtained by the use of copper compounds in the mixture, is one of the richest and most beautiful reds that has ever been obtained in Ceramic work. The art of obtaining the color was well known by the Chinese thousands of years ago but since then it has been lost. At the present time this glaze effect is occasionally obtained, usually by a more or less fortunate regulation of firing conditions that is not well understood.

Although it is admitted by nearly all Ceramists that the glaze should be of the porcelain type, and that the firing conditions should be chiefly reducing, followed by an oxidation period, there is a general disagreement concerning the details of the operation. The subjects of dispute are the raw materials to be used, the frequency and violence of reduction, and the rate of cooling. In order to illustrate the different methods which have been followed with at least partial success a few examples are given below.





THE CHINESE METHOD OF BURNING. ★

The kilns used by the Chinese were rectangular or oval, and narrow toward the ends. The height was very irregular. The atmosphere in such a kiln could not possibly have been as uniform as in our modern kilns. The width, height and length of the Chinese kiln were in the ratio 1 : 1 : 2. In setting these kilns, one or two rows of common vases were placed in the front to check the keenness of the fire. The atmosphere inside of the kilns must have been reducing, for the sea-green vases, which can only be produced under reducing conditions, were placed in the center of the kiln. The kilns were opened and the saggers containing the ware were removed while still at a red heat, the workmen covering their hands and heads with wet linen. The resultant rapid cooling seems to have accounted to some extent for the excellence of their red colors.

Seger<sup>1</sup> obtained some good copper reds by a special heat treatment which he devised. His procedure was to fire with strong reduction up to the melting point of silver, the alternately oxidizing and reducing up to incipient fusion in order to prevent too great a deposit of carbon within the glaze. After fusion an oxidizing fire was maintained until the finish of the burn. This was followed by rapid cooling with the damper open. Open saggers were used for the wares, and wood as fuel.

Lauth and Dutailly in 1879 at Sevres found that the copper red glaze, if allowed to remain in a fluid condition for any considerable length of time would return to the green condition.

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★ Trans. English Cer. Soc. Volume 7, pp. 71.

1. Seger, Collected Writings, pp. 733.



They<sup>1</sup> stated that for this reason large commercial kilns were unsuitable for this sort of ware.

Franchet<sup>2</sup>, a French potter, in 1908, made the ox blood red glaze on a commercial scale, using a down draft kiln of two cubic meters capacity with 3 furnaces. He came to the conclusion that the glaze should contain alkalies, lead and a greater quantity of tin oxide than of the copper compound. His first glaze contained:

White porcelain glaze	----	79 %	by weight.
PbO	-----	10 %	"
CuO	-----	3 %	"
SnO <sub>2</sub>	-----	8 %	"

The glazes were fritted and  $\text{CuC}_2\text{O}_4$  was found preferable as the ingredient for introducing the copper. Contrary to Seger's opinion he found that he could obtain the best results by setting his ware in closed saggars, and offered the explanation that the Cuprous oxide was thus less easily reoxidized to give the green color. The method of burning was also somewhat different, for he reduced strongly up to cone 012 following this by steady oxidation up to cone 10, or maintained reducing conditions for 8 to 9 hours followed by 12 hours of oxidation. More than 16 hours of oxidation caused some of his pieces to turn green, and with 25 hours of oxidation a red glaze was an exception. He also advocated cooling the glaze as quickly as possible. This statement applies to large kilns

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1. Trans. English Cer. Soc. Volume 7, pp. 75.

2. Trans. English Cer. Soc. Volume 7, pp. 71.





which naturally cool slowly.

Some good ox blood reds have also been obtained by Henbach<sup>1</sup>, his best glazes being developed between cones 4 and 7 by firing in a manner similar to that of Seger.

In 1912, Otto Springe, experimented with the copper red glaze and obtained some good smooth reds although light in color. He found that the critical temperature, below which the copper red could not be formed was between  $950^{\circ}$  and  $1000^{\circ}\text{C}$ . His glazes were first burned to maturity under oxidizing conditions and after cooling were reburned with strong reduction alternated with oxidation between the temperatures  $900^{\circ}$  and  $1050^{\circ}\text{C}$ .

This method was fairly certain to produce red colors but did not allow the use of lead and at its best gave only a surface reduction. He concluded that some alkalies should be present in order to give the glaze life and luster and found that illuminating gas gave the best deposit of free carbon upon the glaze.

A. E. Williams<sup>2</sup>, in experimenting upon the copper ruby glass, adopted the newer and more modern theory that the copper in the red glass or glaze exists as a free metallic colloid rather than as the cuprous oxide, as was assumed by the earlier investigators. Following this theory, the glazes should be cooled as slowly as possible without becoming green, since colloids increase

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1. Trans. Am. Cer. Soc. Volume II, pp. 48.

2. Thesis, Library, University of Illinois.



in size with slow cooling, while rapid cooling causes them to remain so small that they are invisible

Below are a few formulae and batch weights of glazes which have given good copper red colors.

Chinese Red. Glazes Good at 1300°C.

Batch weights.

Calculated Formulae.

	(I)	(II)		(I)
Pegmatite -----	40	40	.0549 K <sub>2</sub> O )	
Sand -----	40	44	.0829 Na <sub>2</sub> O )	.285 Al <sub>2</sub> O <sub>3</sub> ) 4.85 SiO <sub>2</sub> .
Chalk -----	18	12	.8200 CaO )	.498 B <sub>2</sub> O <sub>3</sub> ) .017 SnO <sub>2</sub> .
Borax -----	12	--	.0105 MgO )	
CuO -----	6	6	.0318 CuO )	
Soda -----	--	24.5		(II)
SnO <sub>2</sub> -----	6	3	.0600 K <sub>2</sub> O )	
			.7060 CaO )	5.82 SiO <sub>2</sub> .
			.188 Na <sub>2</sub> O )	.312 Al <sub>2</sub> O <sub>3</sub> ) .19 SnO <sub>2</sub> .
			.012 MgO )	
			.035 CuO )	

Chinese Dark Red. Developed by Seger<sup>1</sup>.

White porcelain glaze --	75.00	.217 K <sub>2</sub> O )	
CuO -----	.15	.142 Na <sub>2</sub> O )	.364 Al <sub>2</sub> O <sub>3</sub> ) 3.62 SiO <sub>2</sub> .
SnO <sub>2</sub> -----	1.00	.506 CaO )	.142 B <sub>2</sub> O <sub>3</sub> )
Fe <sub>2</sub> O <sub>3</sub> -----	.50	.128 BaO )	.0108 Fe <sub>2</sub> O <sub>3</sub> ) .023 SnO <sub>2</sub> .
		.006 CuO )	
Barium Glass )	.5 Na <sub>2</sub> O )	2.5 SiO <sub>2</sub> )	
			23.35
	.5 BaO )	.5 B <sub>2</sub> O <sub>3</sub> )	

1. Seger, Collected Writings, pp. 735.

Table 1. Clinical features of the patients.			
Patient	Age	Sex	Duration of illness
1	45	M	10 years
2	52	F	15 years
3	38	M	8 years
4	60	F	20 years
5	42	M	12 years
6	55	F	18 years
7	35	M	5 years
8	48	F	14 years
9	50	M	16 years
10	40	F	11 years
11	58	M	22 years
12	44	F	9 years
13	51	M	17 years
14	39	F	7 years
15	53	M	19 years
16	46	F	13 years
17	54	M	21 years
18	41	F	10 years
19	56	M	18 years
20	43	F	12 years
21	59	M	23 years
22	47	F	14 years
23	52	M	17 years
24	40	F	11 years
25	57	M	20 years
26	45	F	13 years
27	50	M	16 years
28	42	F	10 years
29	55	M	19 years
30	44	F	12 years
31	51	M	17 years
32	39	F	7 years
33	53	M	19 years
34	46	F	13 years
35	54	M	21 years
36	41	F	10 years
37	56	M	18 years
38	43	F	12 years
39	59	M	23 years
40	47	F	14 years
41	52	M	17 years
42	40	F	11 years
43	57	M	20 years
44	45	F	13 years
45	50	M	16 years
46	42	F	10 years
47	55	M	19 years
48	44	F	12 years
49	51	M	17 years
50	39	F	7 years
51	53	M	19 years
52	46	F	13 years
53	54	M	21 years
54	41	F	10 years
55	56	M	18 years
56	43	F	12 years
57	59	M	23 years
58	47	F	14 years
59	52	M	17 years
60	40	F	11 years
61	57	M	20 years
62	45	F	13 years
63	50	M	16 years
64	42	F	10 years
65	55	M	19 years
66	44	F	12 years
67	51	M	17 years
68	39	F	7 years
69	53	M	19 years
70	46	F	13 years
71	54	M	21 years
72	41	F	10 years
73	56	M	18 years
74	43	F	12 years
75	59	M	23 years
76	47	F	14 years
77	52	M	17 years
78	40	F	11 years
79	57	M	20 years
80	45	F	13 years
81	50	M	16 years
82	42	F	10 years
83	55	M	19 years
84	44	F	12 years
85	51	M	17 years
86	39	F	7 years
87	53	M	19 years
88	46	F	13 years
89	54	M	21 years
90	41	F	10 years
91	56	M	18 years
92	43	F	12 years
93	59	M	23 years
94	47	F	14 years
95	52	M	17 years
96	40	F	11 years
97	57	M	20 years
98	45	F	13 years
99	50	M	16 years
100	42	F	10 years



Chinese Light Red. Developed by Seger.

Batch weights.

Calculated Formulae.

White porcelain glaze	-----	70.00	.216 K <sub>2</sub> O	)					
Kaolin	-----	5.00	.145 Na <sub>2</sub> O	)	.433 Al <sub>2</sub> O <sub>3</sub>	)	3.76 SiO <sub>2</sub>		
CuO	-----	1.0-.5	.489 CaO	)	.146 B <sub>2</sub> O <sub>3</sub>	)	.04 SnO <sub>2</sub>		
SnO <sub>2</sub>	-----	2.0	.0464 CuO	)					
			.0232	)					
Barium Glass	)	.5 Na <sub>2</sub> O	)	2.5 SiO <sub>2</sub>	)				
	)	.5 Ba O	)	.5 B <sub>2</sub> O <sub>3</sub>	)	22.0			

Chinese Blood Red Glaze (from analysis)

.072	K <sub>2</sub> O	)							
.210	Na <sub>2</sub> O	)	.203	Al <sub>2</sub> O <sub>3</sub>	)				
.489	CaO	)			)	2.45	SiO <sub>2</sub> .		
.105	MgO	)			)	.05	SnO <sub>2</sub> .		
.091	PbO	)	.0217	Fe <sub>2</sub> O <sub>3</sub>	)				
.037	CuO	)			)				

Chinese Blood Red Glaze.

Batch Weights.

Calculated Formula.

SiO <sub>2</sub>	-----	59.6							
SnO <sub>2</sub>	-----	.32							
CuO	-----	1.20	.072	K <sub>2</sub> O	)				
PbO	-----	8.2	.21	Na <sub>2</sub> O	)	.203	Al <sub>2</sub> O <sub>3</sub>	)	
Fe <sub>2</sub> O <sub>3</sub>	-----	1.4	.489	CaO	)			)	2.45 SiO <sub>2</sub> .
Al <sub>2</sub> O <sub>3</sub>	-----	8.4	.105	MgO	)			)	.493 SnO <sub>2</sub> .
CaO	-----	11.1	.091	PbO	)	.022	Fe <sub>2</sub> O <sub>3</sub>	)	
MgO	-----	1.7	.037	CuO	)			)	
Na <sub>2</sub> O	-----	5.27							
K <sub>2</sub> O	-----	2.74							



Otto Springe's Best Copper Red.

.29	K <sub>2</sub> O	)		
.448	CaO	)	.39	Al <sub>2</sub> O <sub>3</sub>
.19	BaO	)		3.2 SiO <sub>2</sub> .
.05	Na <sub>2</sub> O	)		.05 SnO <sub>2</sub> .
.02	CuO	)	.10	B <sub>2</sub> O <sub>3</sub>

## OBJECT AND SCOPE OF THIS WORK

The following experiments were made more for the purpose of establishing definite rules for the behavior of the copper red glaze during burning, than for the purpose of developing a new formula. This work if carefully performed should solve the reasons for at least some of the mysterious accidents that have been the cause of the ox blood red glaze. It would be impossible in so small a number of experiments to develop a copper red glaze to perfection; hence that is not the purpose of this thesis.

## METHOD OF PROCEDURE

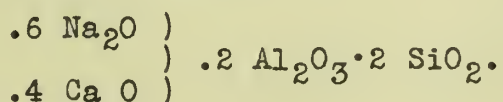
Since it is generally admitted that the development of the red color with copper depends more upon the firing conditions than upon the composition, it was decided to try the effects of various methods of preparation and burning a few of the above glazes in order to determine the most satisfactory treatment. Accordingly, six of these were chosen, representing each type of the red glaze. Since there appeared to be no advantage in fritting the entire glazes separately, a scheme was devised by which the fritting might be mini-



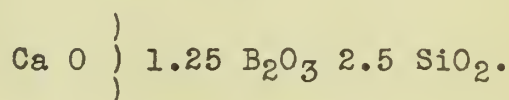


mized. Four mixtures were made from materials that passed a 100 mesh screen. Each frit was thoroughly mixed by sifting through a 60 mesh screen; and then fused in a drop fritt crucible, ground dry in a porcelain ball mill for five hours and screened through a 100 mesh sieve. The remaining materials for the five glazes were passed through the 100 mesh screen, and the glaze mixtures ground dry for two hours, after which they were again screened through the 100 mesh sieve. These glazes and all others in these experiments were applied to biscuit tile furnished by the U. S. Encaustic Tile Company. The batch weights and formulae of the four frits and five glazes were as follows:

Frit 1.



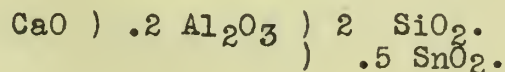
Frit 2.



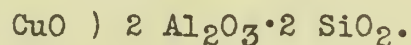
Soda ash -----	6.36
Whiting -----	4.00
N. C. Kaolin -----	5.16
Flint -----	9.60

Whiting -----	10
Crystallized $H_3BO_3$ ----	24.25
Flint -----	15

Frit 3.



Frit 4.



Whiting	-----	10
N. C. Kaolin	-----	5.16
Flint	-----	9.60
Tin oxide	-----	7.55

CuO	-----	8.00
N. C. Kaolin	-----	5.16
Flint	-----	9.60



GLAZE A

Batch Weights.		Formula.			
Frit 1	47.3				
Potash Spar	121				
BaCO <sub>3</sub>	25.2				
Black copper oxide	2.4	.217 K <sub>2</sub> O	)		
Frit 2	33.3	.142 Na <sub>2</sub> O	)	.364 Al <sub>2</sub> O <sub>3</sub>	3.62 SiO <sub>2</sub> .
Frit 3	12.5	.506 Ca O	)	.142 B <sub>2</sub> O <sub>3</sub>	
Fe <sub>2</sub> O <sub>3</sub>	1.73	.128 Ba O	)	.0108 Fe <sub>2</sub> O <sub>3</sub>	.023 SnO <sub>2</sub> .
CaCO <sub>3</sub>	25.2	.030 Cu O	)		
English Ball Clay-	23.45				
Flint	77				
Raw borax	5				

GLAZE B

Potash spar	120				
Frit 1	48.3				
BaCO <sub>3</sub>	25.6	.216 K <sub>2</sub> O	)		
Frit 2	34.2	.145 Na <sub>2</sub> O	)	.433 Al <sub>2</sub> O <sub>3</sub>	3.76 SiO <sub>2</sub> .
Frit 3	27.19	.489 CaO	)		
Frit 4	6.61	.130 BaO	)	.146 B <sub>2</sub> O <sub>3</sub>	.05 SnO <sub>2</sub> .
Whiting	17.50	.030 CuO	)		
English C. clay --	36.9				
Flint	70				
Borax	5				



GLAZE C

Batch Weights.		Formula.			
Potash spar	30.5				
Frit 1	27.6				
MgCO <sub>3</sub>	.883				
Frit 2	117	.0549 K <sub>2</sub> O	)		
Frit 3	90.8	.0829 Na <sub>2</sub> O	)	.285 Al <sub>2</sub> O <sub>3</sub>	
Frit 4	7.01	.8200 CaO	)		4.85 SiO <sub>2</sub> .
Whiting	5.1	.0105 MgO	)	.498 B <sub>2</sub> O <sub>3</sub>	.017 SnO <sub>2</sub> .
English C. clay	33.6	.0318 CuO	)		
Flint	134				
Raw Borax	5				

GLAZE D

Potash spar	65.6				
Frit 1	51.7				
Frit 3	54.38				
Black copper oxide	17.2	.118 K <sub>2</sub> O	)		
Whiting	15.8	.185 Na <sub>2</sub> O	)	.218 Al <sub>2</sub> O <sub>3</sub>	
Fe <sub>2</sub> O <sub>3</sub>	7.68	.481 CaO	)		4.55 SiO <sub>2</sub> .
Flint	169	.215 CuO	)	.048 Fe <sub>2</sub> O <sub>3</sub>	.10 SnO <sub>2</sub> .
Glue	10				
Borax	5				





GLAZE E

Batch Weights.		Formula.			
Raw borax -----	5				
Glue -----	10				
Spar -----	77.8	.14 K <sub>2</sub> O )			
Frit 1 -----	40	.12 Na <sub>2</sub> O )	.18 Al <sub>2</sub> O <sub>3</sub> )		
MgCO <sub>3</sub> -----	4.2	.25 CaO )		2.4 SiO <sub>2</sub> .	
Zinc oxide -----	4.05	.05 MgO )	.		
Red lead -----	73	.05 ZnO )		.05 SnO <sub>2</sub> .	
Copper oxide (CuO) -	5.6	.32 PbO )	.12 B <sub>2</sub> O <sub>3</sub> )		
Frit 2 -----	28.2	.07 CuO )			
CaCO <sub>3</sub> -----	7.4				
Flint -----	55.2				
SnO <sub>2</sub> -----	7.56				

GLAZE F

Potash spar -----	161				
Frit 1 -----	16.7				
BaCO <sub>3</sub> -----	37.5	.29 K <sub>2</sub> O )			
CuO -----	1.76	.448 CaO )	.39 Al <sub>2</sub> O <sub>3</sub> )	3.2 SiO <sub>2</sub> .	
Frit 2 -----	23.50	.190 BaO )		.05 SnO <sub>2</sub> .	
CaCO <sub>3</sub> -----	23.50	.050 Na <sub>2</sub> O )	.1 B <sub>2</sub> O <sub>3</sub> )		
English B. clay ----	16.3	.022 CuO )			
Flint -----	41				
Frit 3 -----	27.19				
Raw borax -----	5				

TRANS AM CER SOC VOL XVII

FIG 5

STULL & HURSH

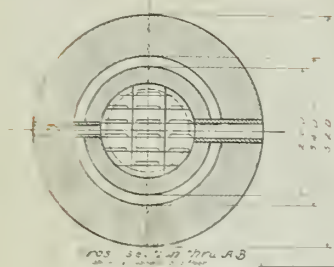
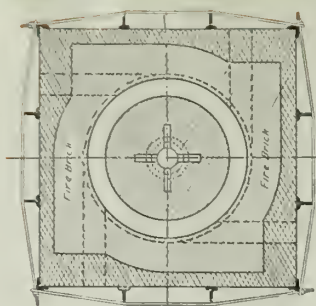
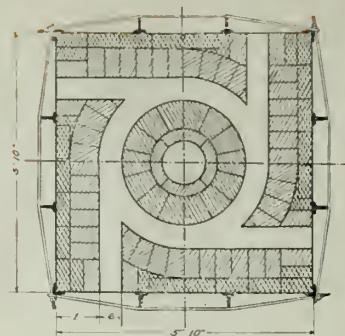


FIG 5 - 1/2" THRU A-B

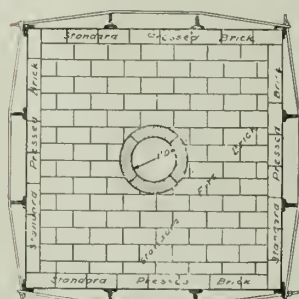
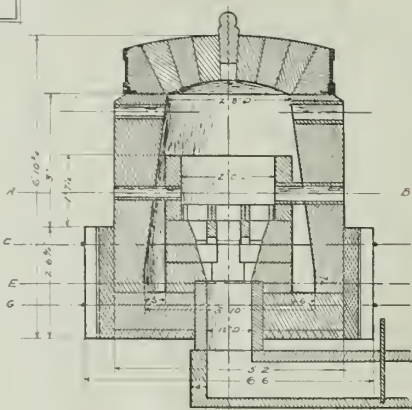
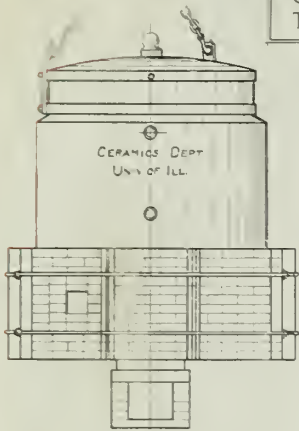
OIL FIRED  
TEST KILN



Cross section thru C-D  
showing opening into fire



Cross section thru E-F



Cross section thru G-H

Oil Fired Test Kiln



Gas Fired Test Kiln

## BURN ONE

This burn was made in a small gas open fire test kiln as shown on the preceding page, following Springe's method as closely as possible. Steady oxidation was maintained up to  $850^{\circ}\text{C}$ ; then alternately violent reduction and oxidation in periods of 15 minutes each were maintained up to  $1150^{\circ}\text{C}$ . This was followed by steadily oxidizing conditions until cone 6 went down. The total duration of the burn being 12 hours.

## RESULTS OF BURN ONE

Glaze A - Flaked and bubbled slightly. The copper separated out as the red cuprous oxide, giving a speckled effect with a green background.

Glaze B - Flaked; color bluish green.

Glaze C - Blistered. A slight reddish tinge appeared in spots.

Glaze D - Flaked; black and metallic, due to too high content of copper.

Glaze E - Smooth, medium green.

Glaze F - Greenish blue, a little flaked; good smooth texture. Some of the copper separated out as a red speckle.

Evidently this method did not give the proper treatment.

From the results the conclusion was drawn, that the copper separated out because it had not been fritted with the entire glaze, that the flaking was undoubtedly due to too high a content of raw clay, and that the copper red did not develop because the reduction was not violent enough to deposit carbon particles within the glazes.

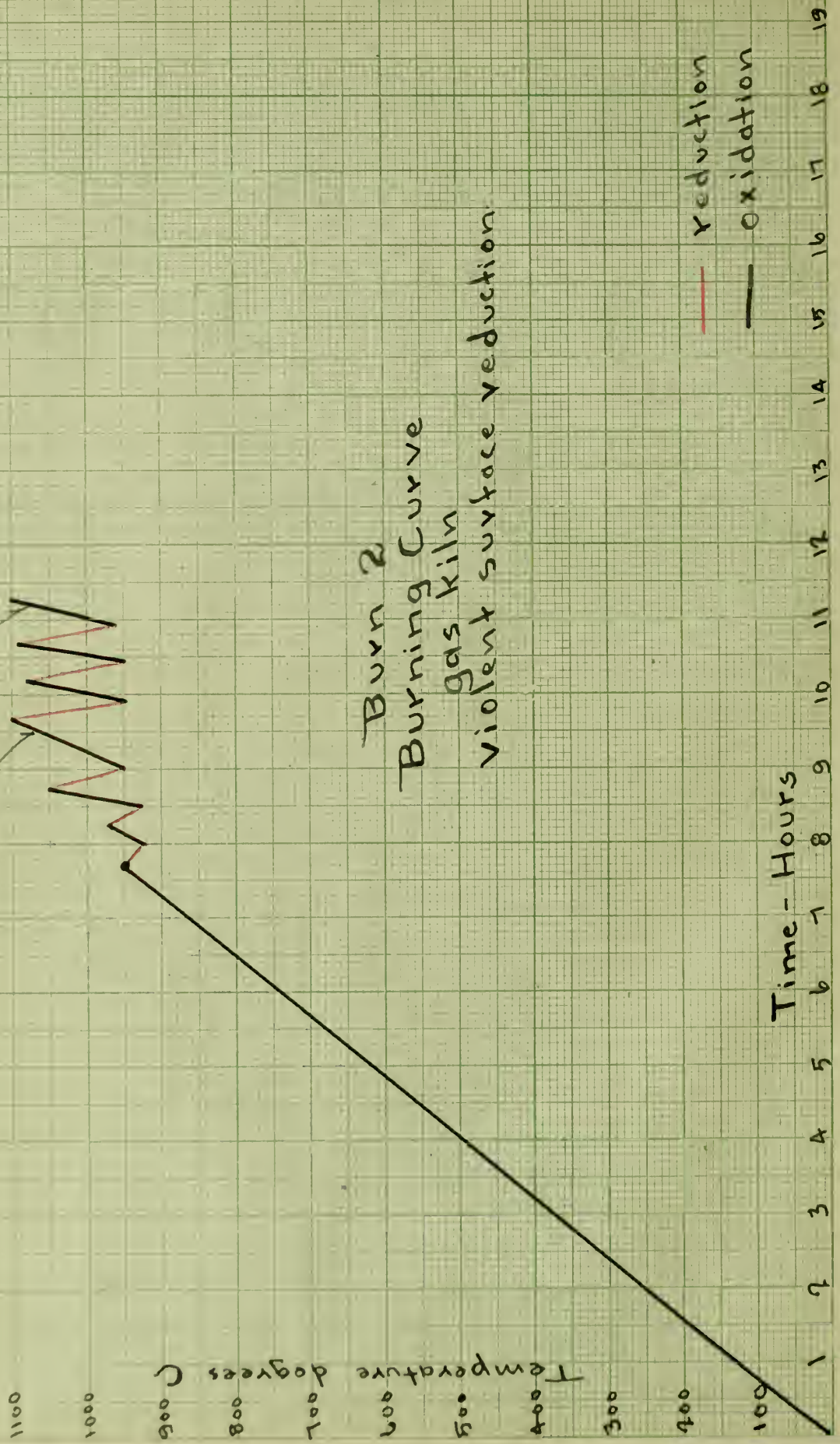


2nd draw  
good red

1st draw  
weak red

Burn 2  
Burning Curve  
gas kiln  
violent surface reduction

— reduction  
— oxidation





## BURN TWO

This experiment consisted of two burns, the trial pieces being first burned under steadily oxidizing conditions to cone 6, then reburned under violently reducing conditions, obtained by pouring fuel oil inside the kiln during the firing. The procedure of this burn is illustrated by the curve on the preceding page. At the finish of the burn, the damper was opened wide, and the kiln was allowed to cool to room temperature in eight hours.

## RESULTS OF BURN TWO

Glaze A - Good opaque red.

Glaze B - Dark rich Indian red. This glaze had been dipped thick.

Glaze C - Red with blackish shade due to over-reduction.

Glaze D - Black and blistered.

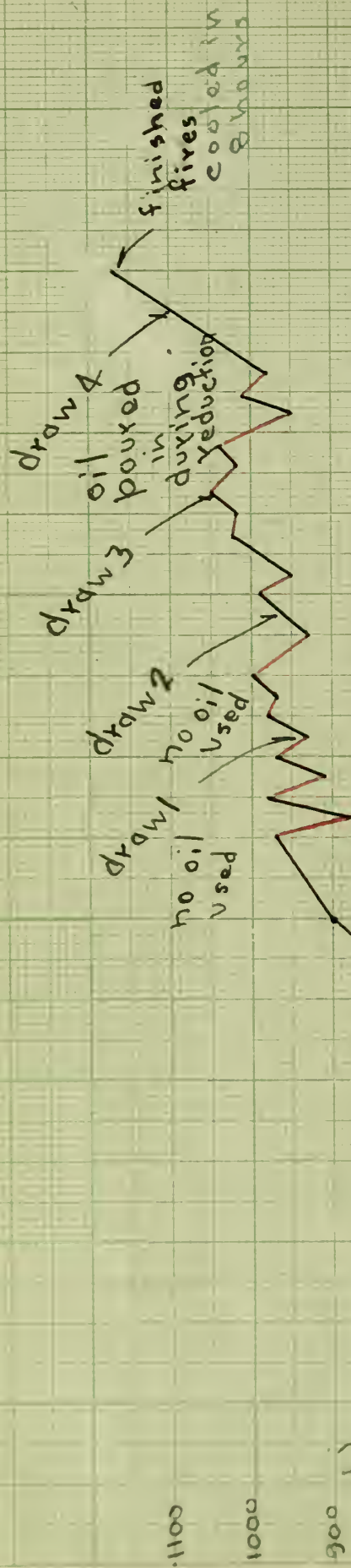
Glaze E - Green, with a few red spots. Blistered.

Glaze F - With 45 minutes reduction was a smooth light red; with 90 minutes reduction was reddish black.

All of the above glazes except those in which no raw clay was used had flaked to some extent. To avoid beading and flaking, the same glazes were remade, using only .05 equivalent of raw clay, introduced as English China clay, and an addition of 2% of raw borax. These were burned in the gas kiln under steadily oxidizing conditions to cone 6. As a result all produced smooth, green glazes of commercial quality, free from beading or flaking.

## BURN THREE

This burn was also made in the gas fired test kiln, using closed saggars and draw trials. Fuel oil was poured into the kiln



# Burn 3 Burning Curve Gas fired Test Kiln

violent surface reduction

— reduction  
— oxidation

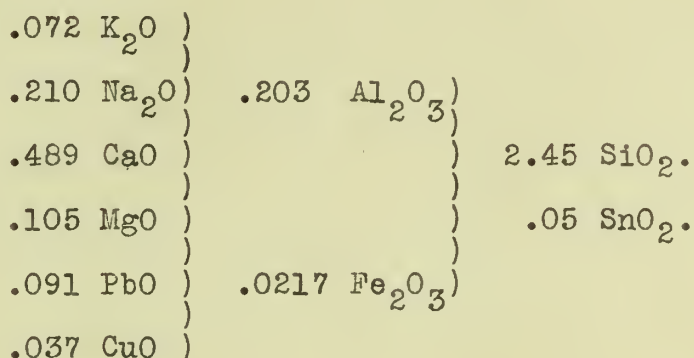
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19



to obtain as violent reduction as possible. The burning record is shown on the preceding page, and illustrates how three distinct methods of reduction were tried: one at 900°C, one at 950°C and one at 1000°C.

### RESULTS OF BURN THREE

Draw 1, was glaze G, one of the blood red Chinese glazes having the formula,



Under the moderate reduction which it received, it produced a light red.

Draw 2, (Glaze A). The color was gray, with just a trace of red.

Draw 3, (Glaze G). Still there was only a tinge of red.

Draw 4, (Glaze B). This was a strong red, but was blistered due to too long continued reduction, which allowed too much carbon to become imbedded within the glaze, and also to reduction at too high a temperature.

The trials in the saggars were all gray but Glaze G, which was a mixture of red and black.

### CONCLUSIONS FROM BURN THREE

This burn proved that leadless glazes could not be reduced to the red color unless carbon was actually deposited on the trial.

1st drop  
2nd drop  
3rd drop  
4th drop  
5th drop  
6th drop  
7th drop  
8th drop  
9th drop  
10th drop  
11th drop  
12th drop  
13th drop  
14th drop  
15th drop  
16th drop  
17th drop  
18th drop  
19th drop  
20th drop  
21st drop  
22nd drop  
23rd drop  
24th drop  
25th drop  
26th drop  
27th drop  
28th drop  
29th drop  
30th drop  
31st drop  
32nd drop  
33rd drop  
34th drop  
35th drop  
36th drop  
37th drop  
38th drop  
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42nd drop  
43rd drop  
44th drop  
45th drop  
46th drop  
47th drop  
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49th drop  
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80th drop  
81st drop  
82nd drop  
83rd drop  
84th drop  
85th drop  
86th drop  
87th drop  
88th drop  
89th drop  
90th drop  
91st drop  
92nd drop  
93rd drop  
94th drop  
95th drop  
96th drop  
97th drop  
98th drop  
99th drop  
100th drop

Burn 4  
Burning Curve

gas kiln  
violent surface reduction

— reduction  
— oxidation

time in hours

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19

temperature degrees C.  
1100  
1000  
900  
800  
700  
600  
500  
400  
300  
200  
100



Glazes containing a little lead, however, behave differently and show red colors under moderate reduction. It also showed that the temperature during the reduction period must be above  $950^{\circ}$  or the copper will not produce the red color; and that it must be kept below  $1000^{\circ}$  or the carbon will sink too deeply into the glaze and cause blistering.

#### BURN FOUR. GLAZE A,B,F, AND G.

The glazes, which had previously been burned to a smooth green were this time burned again in a similar manner to Burn 3 as shown by the curve on the preceding page, except that this time the saggars were left partially open, and as violent a reduction as possible was maintained during the critical temperature interval. The cooling was as fast as possible.

#### RESULTS OF BURN FOUR

Glaze A - Strong smooth red.

Glaze B - Green with black spots, no red.

Glaze F - Draw trial was a good smooth red.

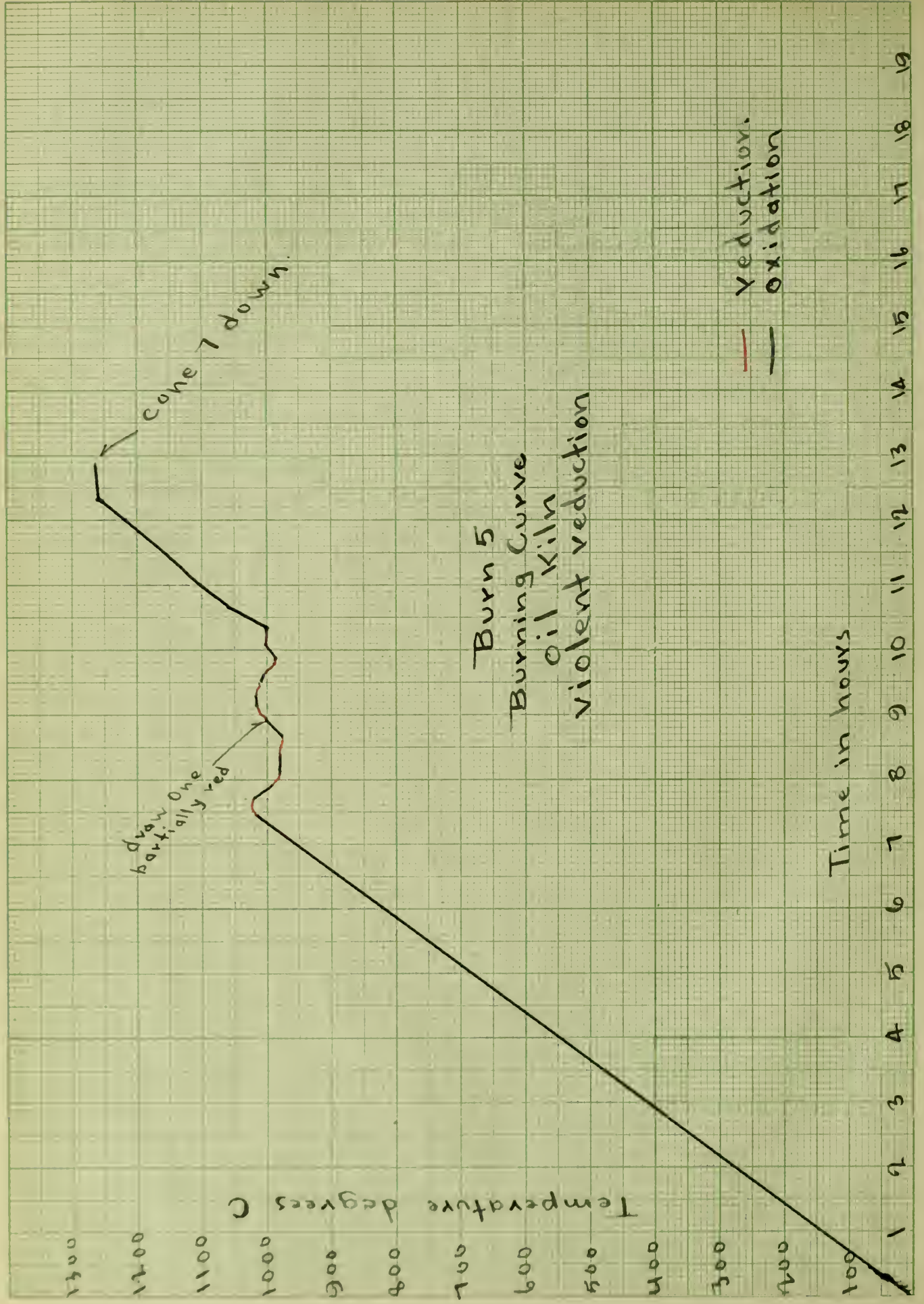
Glaze G - Light red, but a little rough.

Since there is practically no difference in composition between Glaze A and Glaze B, except that a little  $\text{Fe}_2\text{O}_3$  is present in A, it must be assumed that iron is instrumental in helping the formation of the copper red. The results show a general improvement over Burn 3, on account of the open saggars, and the shorter period of reduction.

#### BURN FIVE

It was decided to again try burning the copper glaze





Burn 5  
Burning Curve  
oil Kiln  
violent reduction

without having either fritted it altogether or burned it in an oxidizing flame. This time a larger kiln, as shown on page 11a was used, burning with fuel oil. Since this kiln was much more easily controlled and the temperature could be raised faster, the results should be better. In this burn Glazes A, B, and F were tried, since they had given the best previous results. The burning curve is shown on page 15a.

#### RESULTS OF BURN FIVE

The draw trial, although only partially red, was the best one of all. The glazes were in the same condition as in Burn 1, being green with a few specks of red, where the copper had separated out. Thus it is seen that fritting is an absolute necessity for single fired glazes. A few trials which had been previously burned to a green color, were also tried in this burn, but were unaffected because the reduction could not be made violent enough for dark surface reds.

Thus far, none of the reds had been as dark or as rich in color as the famous Range Flanke Chinese reds. One reason for this was that the successful reduction so far had been of a surface character only. This was proven by scraping off a little of the surface and disclosing the green background. Although Springe had found repeatedly that poor results were obtained by reduction before fusion had taken place, yet it had been successfully done by the Chinese and by Seger.

It is a well known fact that ruby glass can be made by reducing the copper with one-half percent of cream of tartar. This





suggested the trial of a series of glaze mixtures made up with varying proportions of reducing agents. Glaze B was selected for the purpose and several series of mixtures of the glaze with varying amounts of different reducing agents were made. The entire glaze was first fritted with the following variations in the raw mixture,-

- (1) One-half percent Cream of tartar was added.
- (2)  $\text{SnCl}_2$  instead of  $\text{SnO}_2$ .
- (3)  $\text{Cu}_2\text{O}$  instead of  $\text{CuO}$ .
- (4)  $\text{CuC}_2\text{O}_4$  instead of  $\text{CuO}$ .
- (5) One percent  $\text{Fe}_2\text{O}_3$  was added.

These five batches were melted in drop frit crucibles. Since a reducing atmosphere could not be maintained in the furnace, all of the above frits were green. These, being now of exactly the same composition, were ground together and sifted through a 100 mesh screen. The following additions of reducing agents were then made, to portions of the glaze:

- Series 1.- Glaze B + 1/2, 1, 2, 3, 4, 5, 6, 7, 8, 9  
and 10% of cream of tartar.
- Series 2.- Glaze B + 1/2, 1, 2, 3, 4, 5, 6, 7, 8, 9  
and 10% of soft coal.
- Series 3.- Glaze B + 1/2, 1, 2, 3, 4, 5, 6, 7, 8, 9  
and 10% of flour.

At the same time a glaze was made and fritted which had the following composition:





GLAZE H

Batch Weights.			Formula.		
Potash spar	-----	78			
Soda ash	-----	12.7			
Whiting	-----	5	.13	$K_2O$	)
$MgCO_3$	-----	4.2	.11	$Na_2O$	)
Zinc Oxide	-----	4.05	.05	$CaO$	)
Red lead	-----	118.5	.05	$MgO$	)
$Cu_2O$	-----	7.1	.05	$ZnO$	)
English C. clay	----	8.88	.51	$PbO$	)
$H_3BO_3$ (flaky)	-----	23.3	.10	$CuO$	)
SnO	-----	6.75			
Flint	-----	88.8			

Series 4.- Glaze B + 1% cream of tartar blended with  
Glaze H + 1% cream of tartar.

Series 4.											
Number	1	2	3	4	5	6	7	8	9	10	11
Glaze B	10	9	8	7	6	5	4	3	2	1	0
Glaze H	0	1	2	3	4	5	6	7	8	9	10

Series 5.- Glaze B blended with Glaze H, as above, but  
omitting the cream of tartar.

These glazes were dipped thick, using no adhesive whatever, without any trouble from flaking. They were set in open saggars in the kiln without previously burning to the green color. Along with these glazes were also put the raw mixtures of glaze H, Glaze I, and

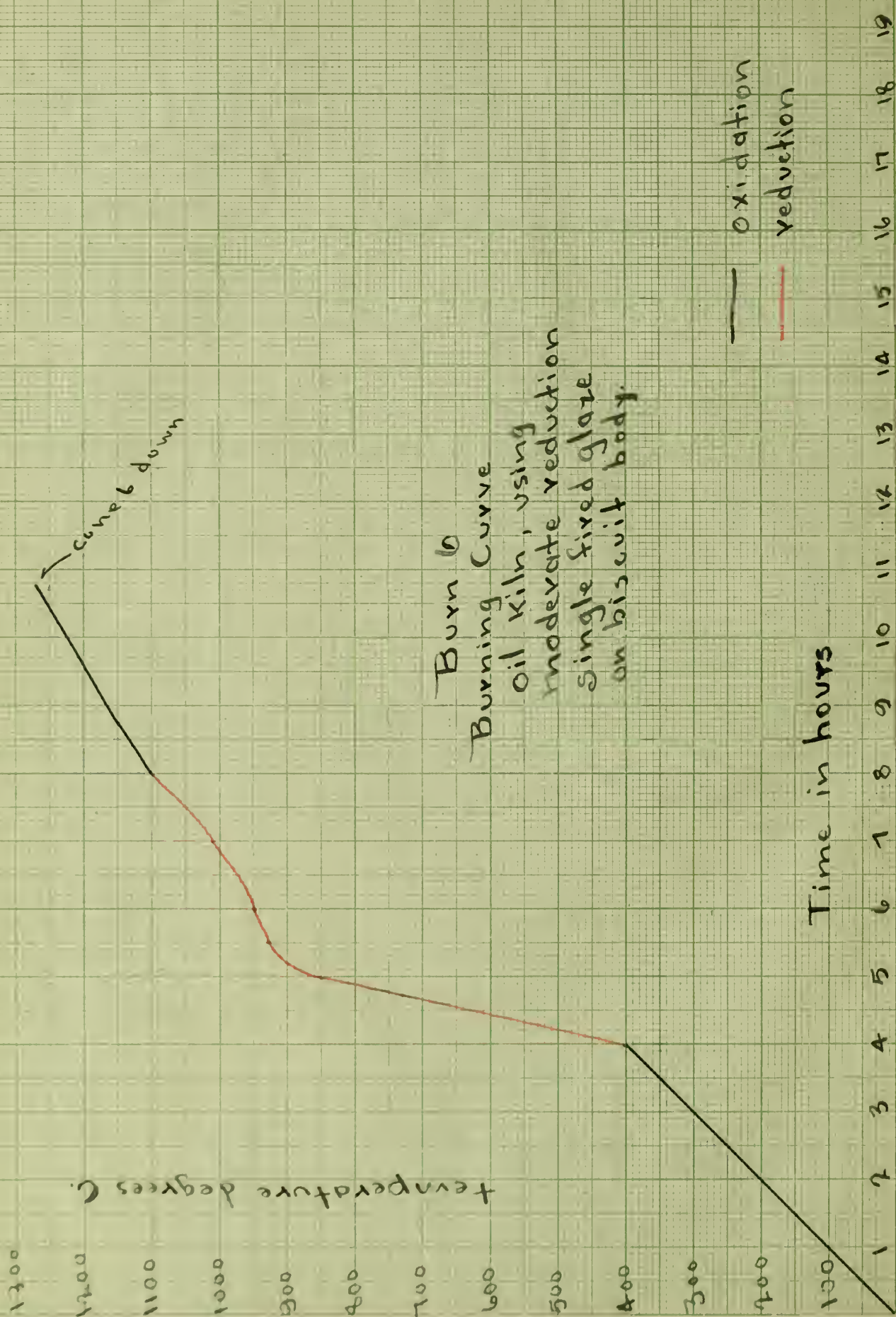
Temperature degrees C.

Time in hours

— oxidation  
— reduction

cone 6 down

Burn 6  
Burning Curve  
oil kiln, using  
moderate reduction  
single fired glaze  
on biscuit body.





Glaze J, each in a separate crucible with one-half percent cream of tartar.

Formula, Glaze I.

.216	K <sub>2</sub> O	)			
.145	Na <sub>2</sub> O	)	433	Al <sub>2</sub> O <sub>3</sub>	)
.489	CaO	)			)
.130	BaO	)	146	B <sub>2</sub> O <sub>3</sub>	)
.100	CuO	)			)
			3.76	SiO <sub>2</sub>	
			.05	SnO <sub>2</sub>	

Formula, Glaze J.

.14	K <sub>2</sub> O	)			
.12	Na <sub>2</sub> O	)	.18	Al <sub>2</sub> O <sub>3</sub>	)
.17	CaO	)			)
.05	MgO	)	.12	B <sub>2</sub> O <sub>3</sub>	)
.52	PbO	)			)
			2.4	SiO <sub>2</sub>	

Batch Weights.

Potash spar	-----	120
Soda Ash	-----	15.4
Whiting	-----	48.9
BaCO <sub>3</sub>	-----	25.6
Cu <sub>2</sub> O	-----	2.14
English China clay	--	56
Flint	-----	122
SnO <sub>2</sub>	-----	7.55
Flaky H <sub>3</sub> BO <sub>3</sub>	-----	28.2
Cream of tartar	----	2.14

Batch Weights.

Potash spar	-----	78
Soda ash	-----	12.7
Whiting	-----	17
MgCO <sub>3</sub>	-----	4.2
ZnO	-----	4.05
Red lead	-----	118.5
English China clay	-----	8.88
Flaky H <sub>3</sub> BO <sub>3</sub>	-----	93.3
Cream of tartar	-----	1.62
Flint	-----	88.8

These glazes and frits were burned in the oil kiln to cone 7, as shown on page 18 a.

RESULTS OF BURN SIX

- Series 1.- Numbers 1, 2, and 3, were reddish black. The others were black. The entire series was beaded.
- Series 2.- These were all black except number 1, which was reddish black.



Series 3.- These were all entirely black except 3-3 which had a red border.

Series 4.- 4-1 was black.

4-2,3, and 4 were brownish black.

4-5 was reddish black.

4-6 was dark red with a few black spots.

4-7 was reddish green.

4-8, 9, and 10 were green.

Series 5.- All were greens. Hence cream of tartar is helpful in producing the reds.

Glaze 4-6 was the nearest to the ox blood red yet obtained being dark and rich in color. With a little higher burning temperature it would make an excellent ox blood red.

Formula of Glaze 4-6.

.173 $K_2O$	)			
.127 $Na_2O$	)			
.265 $CaO$	)	.306 $Al_2O_3$	)	3.03 $SiO_2$ .
.025 $MgO$	)		)	.05 $SnO_2$ .
.025 $ZnO$	)	.133 $B_2O_3$	)	
.065 $BaO$	)			
.255 $PbO$	)			
.065 $CuO$	)			

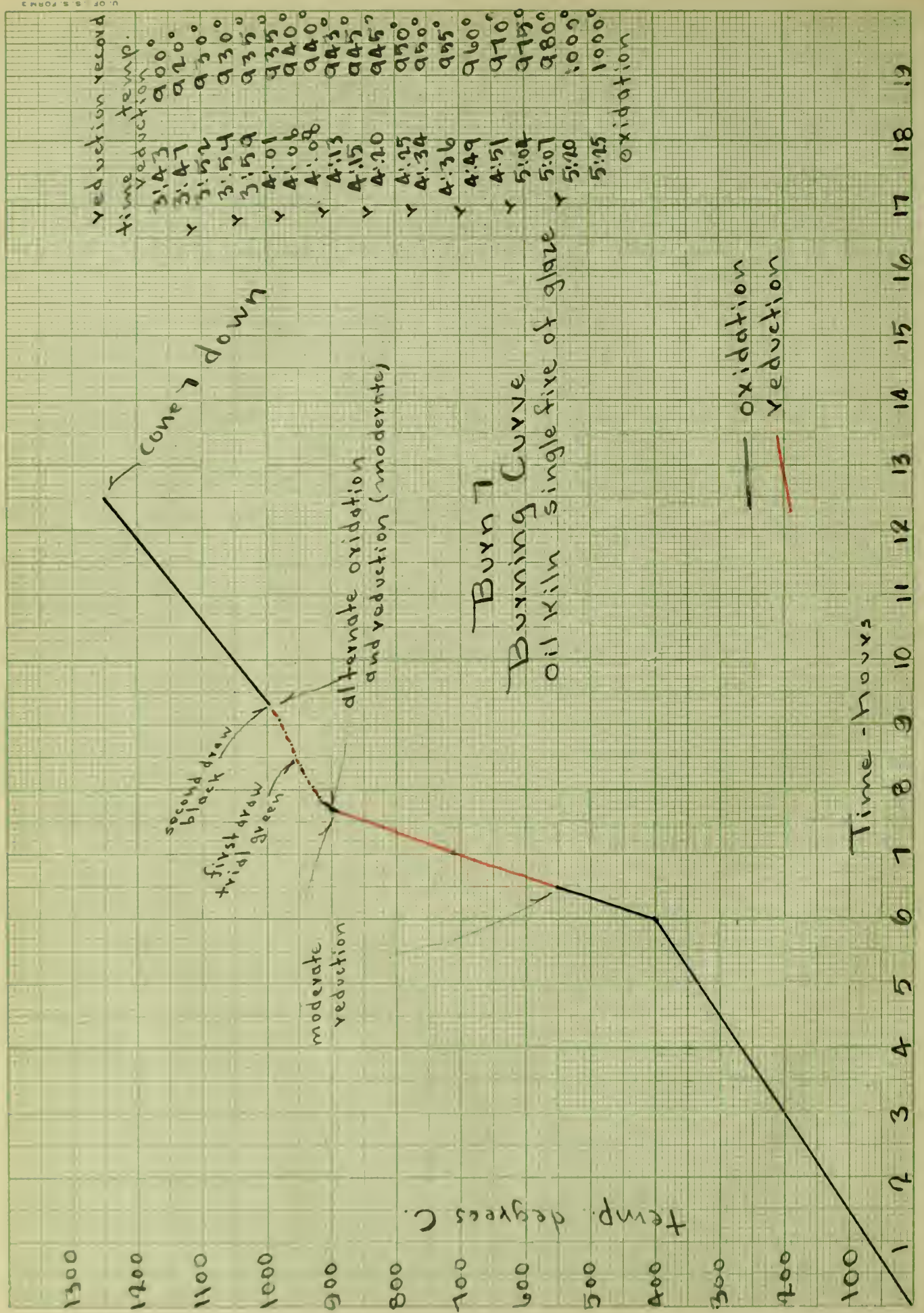
Add 1% cream of tartar.

Frit H burned in the crucible to a dark red, and on shrinking, left a glaze of ox blood red upon the sides of the crucible.

Frit I also burned to a dark red, even stronger in color than frit H.

Frit J burned to a clear white glass.





# CONCLUSIONS FROM BURN SIX

It is evident from this burn that the range of conditions under which the best ox blood red colors can be produced is very small. This burn was too strongly reducing just before fusion, with the result that the carbon was enclosed within the glaze, where it could not burn out without carrying the glaze above its maturing temperature. On the other hand, series 4 shows that those glazes high in lead had lost the red color, due to too high burning temperature, and returned to the green.

## Series 6 and 7.

The frits obtained from burn 6 were ground, screened through the 100 mesh and blended with each other to form two series of glazes.

### Series.6.

Glaze H was blended in the following proportions by weight with Glaze J, adding to each mixture 2% Borax and 1% cream of tartar.

Number	1	2	3	4	5	6	7	8	9	10
Glaze H	2.5	5	7.5	10	12.5	15	17.5	20	22.5	25
Glaze J	22.5	20	17.5	15	12.5	10	7.5	5	2.5	0

### Series 7.

Glaze I was also blended according to parts by weight with Glaze J adding to each mixture 2% Borax and 1% Cream of tartar.

Number	1	2	3	4	5	6	7
Glaze I	5	7.5	10	12.5	15	17.5	20
Glaze J	A-0	17.5	15	12.5	10	7.5	5

These glazes were then burned as shown on page 20d. They were cooled in 10 hours.





Series 6.

Every one of these glazes was smooth and of a green color. Since the temperature of the burn was too high for such a series of glazes the copper had reverted to the green condition.

Series 7.

7 - 1. Slight green.

7 - 2, 7 - 3, and 7 - 4. Medium green.

7 - 5. Green with spots of red.

7 - 6. Strong, dark red but rough texture.

7 - 7. Strong, dark red but a little rough.

These series show definitely that the development of the red colors depends much more upon correct burning treatment than upon composition and also that at temperatures above their maturing point, glazes return very easily to the green condition.

SUMMARY

1. Copper glazes containing lead are much more easily reduced than when lead is absent. When lead is present in the glaze a greater amount of copper must be used to obtain the red color, and when more than .1 equivalent of PbO is present the color readily reverts to the green. Surface reduction can not be successfully applied to glazes containing lead.

2. The presence of iron oxide in the glaze materially aids in the production of the copper-red color.

3. Between the temperatures 950° and 1000° C, fifteen minute periods of reduction are the maximum permissible. More than fifteen minutes of steady reduction is liable to cause blistering





due to too great a deposit of carbon in the glaze. Less than ten minutes of steady reduction is insufficient to develop the red (for surface reduction).

4. The glazes must be completely fritted to produce the true red color.

5. For surface reduction, carbon particles must be deposited on the glaze. It was impossible to do this unless some hydro-carbon was introduced into the kiln while all the openings were closed.

6. Cream of tartar is the best reducing agent. Coal and flour also give fairly satisfactory reduction, but not as good as cream of tartar.

7. Open versus closed saggars. For surface reduction partially open saggars give the better results, while for the complete reduction either open or closed saggars will produce good effects.

8. Reducing the glaze before fusion takes place gives a much darker and richer red than the surface reduction although the former method is more difficult to control.

9. If a series of glazes were prepared covering a wide range of maturing temperatures and burned under strongly reducing conditions between  $950^{\circ}$  and  $1000^{\circ}\text{C}$ , following this by rapid burning under oxidizing conditions up to a definite finishing temperature or until draw trials showed that the carbon had been burned out, at least one or two good red glazes could reasonably be expected.

10. The most efficient time to burn off the carbon is before fusion takes place because the copper-red is more stable at lower temperatures. Since glazes that have been fritted fuse at a much



lower temperature than the raw glazes, it is necessary to keep their composition such that they will not fuse below  $1000^{\circ}\text{C}$ , which is slightly higher than the critical temperature of copper-red. Other wise the carbon will be enclosed within the glaze during reduction and even the development of the red will be prevented, except at the surface. For this reason, glazes of the porcelain type give the most satisfactory results.

11. Glazes which have been applied in a thick coat in dipping show the darker and richer color.

12. The best glazes found during this research were,

Glaze 4 -6. Cone 6.

Glaze 7 - 7. Cone 7.

.173 $\text{K}_2\text{O}$	)		
.127 $\text{Na}_2\text{O}$	)		
.265 $\text{CaO}$	)	.306 $\text{Al}_2\text{O}_3$	} 3.03 $\text{SiO}_2$ .
.025 $\text{MgO}$	)		
.065 $\text{BaO}$	)	.133 $\text{B}_2\text{O}_3$	} .05 $\text{SnO}_2$ .
.255 $\text{PbO}$	)		
.065 $\text{CuO}$	)	Add 1% $\text{KC}_4\text{H}_5\text{O}_6$	

.168 $\text{K}_2\text{O}$	)		
.118 $\text{Na}_2\text{O}$	)		
.451 $\text{CaO}$	)	.318 $\text{Al}_2\text{O}_3$	} 2.92 $\text{SiO}_2$ .
.085 $\text{BaO}$	)		
.010 $\text{MgO}$	)	.118 $\text{B}_2\text{O}_3$	} .032 $\text{SnO}_2$ .
.102 $\text{PbO}$	)		
.066 $\text{CuO}$	)	Add 1% $\text{KC}_4\text{H}_5\text{O}_6$	









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